Bioengineering Research

Enhancing Capillary Force in Glass Microfluidics Devices for Bioengineering Applications

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Abstract

Microfluidic devices have been grown dramatically in recent years. They are widely used in the different fields like biomedicine, cell manipulation, inkjet print heads, molecular biology and DNA analysis. The most important advantages of microfluidic devices are low energy consumption, high precision, low time and low cost. These benefits depend on the performance of fluid motion in microchannels. The major disadvantage of microchannels fabricated on glass or silicon is lack of surface wettability. The fabricated microchannels on glass and silicon substrates cannot transfer water based fluids by surface tension force and usually an external pump is needed to provide enough force to push the fluid along the micro channel. Most of the bio research and applications related to microfluidic devices are working on bio materials which are soluble in water. For bio applications usually it is essential to fabricate hydrophil microstructures while silicon and glass are not hydrophil. Silicon and glass are the most important substrates which are used for MEMS and microfluidic fabrication. So, it will be interesting to enhance hydrophilicity of silicon and glass to be applicable for bio fields. In this paper nanorods are proposed to cover micro channel internal surface in order to enhance hydrophilicity of microfluidic structure. COMSOL is considered as simulation software which is used for simulating fluid motion in microchannels. For evaluation of simulated structure, a star microfluidic structure is fabricated on glass substrate and fluid movement in channels is investigated by experimental setup. The simulated and experimental results show that fabrication of nanorods on internal surface of microchannels would increase capillary force and enhance fluid motion in the channel.

Keywords: Nano rod coating, capillary force, hydrophilicity, biofluidics

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1. Introduction

Microfluidics generally incorporates technology that uses microstructures to manipulate and precisely study liquids, even at thenanoliter and femtoliter scale [1]. Microfluidics technology offer a new generation of identification methods that rely on some steps: sample preparation, reactor manipulation, bioactivity, and identification that can be integrated into a single platform [2]. It can be used to fabricate different parts and connect them to specific and compatible materials with these chips [3-4]. Miniature microfluidics devices have some advantages in the field of chemistry, biology (biochemistry and biomedicine) and medicine. Usually, there are microchannels inside the chips which implement some processes such as mixing, separation, filtration, purification and preparing conditions for chemical and physical reactions. The liquid may carry small particles, such as cells or nanoparticles. Interesting researches have been reported based on microfluidic technology applications in a variety of fields, such as optical detection of pathogens and diseases, surface chemistry, cell separation, cancer detection, cell manipulation, DNA purification and sequencing [2]. In the microfluidic development, they have developed concepts that were originally endorsed in the semiconductor field [5]. Microfluidics is a very interesting technique for academic researchers and industry groups. Most countries today are developing microfluidic technology. More than 250 companies and research teams around the world are working on this field. Microfluidics devices are widely used in the biological sciences because precision controlled experiments can operate at lower cost and at higher speeds. During microfluidics-induced downsizing and automation, one of the following may occur: the precise development of experiments, fewer restrictions on detection and multiple review simultaneously.

Common materials in microfluidic chips are divided into four major groups, silicon based substrates, polymers, hydro jells and paper. Silicon based substrates are very common in microfluidic devices because of common usage with integrated circuit technology. Silicon and glass are two important materials which are used in both IC and MEMS fabrication technology. Most of the fabrication processes for these materials are similar for IC and microfluidic devices fabrication. As second substrate material, polymers are another good option. They can be elastomers (like PDMS), thermosets (like polyimide-su8) or thermoplastics (like PMMA,PC,PS,PET,PVC and TEFF). Each of these polymers has some advantages in comparison with other materials. Two major advantages of polymers are transparency and flexibility. The third substrate material category is hydrogels. One example of hydrogel materials is collagen. Finally, the last substrate material for microfluidics devices is paper. Recently, paper has been introduced as a favorite substrate for biological and medical microfluidic chips. Availability, easy fabrication and lowering the production cost are major factors for growing the research and productions of microfluidic chips with paper substrate.

Elastomers are materials with outstanding flexibility, excellent strength and good thermal conductivity that allow the processes involved in solvent and high-speed capillary electrophoresis [6]. PDMS is suitable for applications in the gaseous environment and are the best materials for the manufacture of integrated valves [7]. Incompatibility with organic solvents and the inability to support some quantitative experiments due to three effects; adsorption of small hydrophobic molecules into the channel walls, adsorption of biomolecules on the channel walls, and variation of soluble concentration through evaporation through the channel walls. On the other side, thermoplastics can be deformed after manufacturing and they can be easily molded and bonded several times with thermal renewal. By appropriate bonding techniques, thermosets can be fully applied to microfluidic chips. Also, Hydrogels such as calcium alginate and gelatin with crosslinks can be used as skeletons of microfluidic devices [8-9].

Paper as a chip material would lead to several benefits. First, the micro-channel acts as a diffuser without the need for external force or components. Second, it can be used for storing reagents by simply drying the wetted area. Also, paper is one of the cheapest materials for microfluidics and printing is inexpensive, too. Finally, paper can be easily stacked and laminated in microfluidic channels.

Silicon and glass are the most important minerals. Due to their resistance to organic solvents, ease of metal deposition, high heat, heat conduction and stable magnetic electrical mobility, the microchannels made of these materials are impervious to gases [10]. Microparticles for the detection of nanomolar or picomolar concentrations of analytics on silicon substrates provide good attraction in biological studies [11-12]. Glass is optically transparent and electrically insulated. Due to its high heat transfer and stable magnetic mobility at its surface, the microchannel on the glass provides higher performance than other material chips. Other important applications of glass and silicon devices are achieved in terms of thermoset and solvent compatibility. As amorphous material, microchannels on glass are manufactured using special etching techniques [13]. Light sensitive glasses can be patterned directly by laser etching [14]. Other important applications of glass and silicon chips are solvent-proof and solvent-based applications. These applications include chip reactions [15], Drop formation [16]and solvent extraction [17]. One of the advantages of glass chips is capability to attach and bond it to PDMS microstructures. The stiffness of glass and silicon also creates limitations for their wide use in these chips. One of their limitations is the manufacture with chemicals such as BHF acid (Buffered Hydrofluoric Acid). And finally, chip grafting is difficult (high temperature, high pressure and extremely clean and clean environments are required) [10]. These limitations have led to the creation and introduction of other materials for these chips that are easily manufactured and are compatible with wider biological applications. One of the most important disadvantages of glass in these chips is its poor capillary against fluids. In the microchannels created on the glass substrate, fluid moves slowly due to the weak capillary force in glass microchannels. It would be useful to propose a process to enhance the capillary force and hydrophilicity of the channel so that the fluid can passively pass over inside the glass microchannels without any external force. In this paper nanorods are deposited on glass microchannel surface in order to enhance capillary force.

2. Nanorods for enhancing the capillary force

Wetness is the ability of a liquid to make contact with a solid surface and is derived from intermolecular forces. The degree of wetting is determined by the balance between the bonding forces and the adhesion. Wetting, in other words, tends to obtain the maximum contact surface for a liquid with its solid surface. The angle of contact of a drop of liquid with its surface is an important parameter. The closer the contact angle is to zero, the higher the wettability. Yang's law defines wettability for an ideal surface:

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG}\, COS\theta \tag{1}$$

Where, $\boldsymbol{\gamma_{SG}}$, $\boldsymbol{\gamma_{SL}}$, $\boldsymbol{\gamma_{LG}}$ are interfacial free energies between the surface of solid-gas, solid-liquid and liquid-gas , respectively. Also, $\boldsymbol{\theta}$ is the contact angle. These studies show that thin films (with thicknesses ranging from a few nanometers to several micrometers) can be used to hydrate the surface [18]. Therefore, for capillary movement within the microfluidic microchannel, the surface of the glass chip must first be hydrophilic so that the fluid can move without any external force. Now to move better and improve fluid velocity with the capillary phenomenon in the microchannel, the fluid moves easily inside the microchannel by growing nanorods inside the microchannel and adjusting the distance between the nanorods. The nanorods surfaces have the potential to increase the surface area in ion exchange and catalytic potential for various applications [19-20]. For the reasons mentioned above, the outer surfaces of these nanorods contribute to the capillary phenomenon and, on the other hand, they are hydrophilic due to being oxidized and attracting fluid molecules, thereby the fluid easily and rapidly moves between nanorods. The motion of the fluid in the microchannel depends on the distance between the nanorods so that the fluid can move freely and without hindrance. The fluid molecules move from nanorod to nanorod, and thus the fluid inside the microchannel on the glass chip can easily flow by the capillary force. As shown in figure 2, at the beginning of fluid entry into the structure, the fluid behavior due to the capillary phenomenon between the two microchannels swirls and then enters the microchannels. This figure shows the actual behavior of nanorods inside the microchannels, which, as soon as the fluid enters without any external force, immediately pulls the fluid toward itself inside the microchannel, which defines the same hydrophilicity and surface behavior. The capillary using nanorods growth inside the microchannel shows how effective the nanorods are in the attraction of fluids to the self (inside the microchannels).

3. Structure Simulation:

Because of software comprehensiveness, this structure was simulated in COMSOL multiphysics version 5.4. In the simulation, the Navier-Stokes equations are used to describe the transport of motion and the conservation of mass. In this simulation, two laminar flow and phase field physics were used. COMSOL's software uses two Cahn-Hilliard equations to describe Navier-Stokes equations.

(2)

$$\frac{\partial \phi}{\partial t} + u\,.\nabla\phi = \nabla.\frac{\lambda\gamma}{\varepsilon^2}.\nabla\psi$$

$$\Psi = -\nabla.\,\varepsilon^2\nabla\phi + (\phi^2 - 1)\phi$$

Where **u** is the fluid velocity **(m / s)**, **ϒ**is the mobility**($\frac{m^3.s}{kg}$)**,**λ**is the mixing energy density of the two fluids **(N)**,**ε**is the thickness parameter of the interface with the surface tension coefficient **(m)** and **ψ** is the auxiliary variable phase field. The diffuse interface is defined as the region where the dimensionless phase field variable$\boldsymbol{\phi}$ goes from -1 to 1.

The following equation is related to the mixing energy density and the interface thickness with the surface tension coefficient.

(3)

$$\sigma = \frac{2\sqrt{2}}{3}\frac{\lambda}{\varepsilon}$$

Normally, the interface thickness parameter can be set to$\boldsymbol{\varepsilon} = \frac{h_c}{2}$where$\boldsymbol{h_c}$is the characteristic mesh size in the area connected by the interface. The structure is made of glass with a microchannel depth of 20 micron, a width of 120 and 170 microns and a microchannel length of 5000 microns. The fluid entering the microchannel is Newtonian fluid which flows well through the microchannels by the capillary force without any external force. In simulation, due to the high number of nanorods and difficulties in meshing high number small surfaces, they are modeled by increasing the capillary surface area and reducing the contact angle between the liquid and the surface. So, the tensile effects of the capillary and the surface are well characterized in the simulation.

In the simulation section to incorporate nanorods into the microchannels, the contact angles of the fluid surface with the microchannel walls were reduced to increase the surface hydrophilicity, as shown in figure 1.

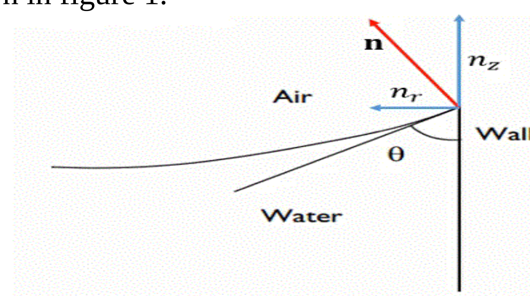

Figure 1. Angular contact angle of the fluid with the microchannel wall

In figure .1, $\boldsymbol{n_r}$, $\boldsymbol{n_z}$and **n** are the radial vector, the perpendicular and normal vectors to the surface. **n** is defined as follows in three spatial dimensions.

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$$n = \frac{\nabla F}{\sqrt{Fx^2+Fy^2+Fz^2}} \tag{4}$$

F represents the force in three different directions. As shown in the figure 2, the fluid through the surface capillary phenomenon reaches 70% of the microchannel length and gradually decreases the fluid pressure and velocity along the microchannel length. Microchannel width also has a significant effect on the capillary and fluid surface tensions.

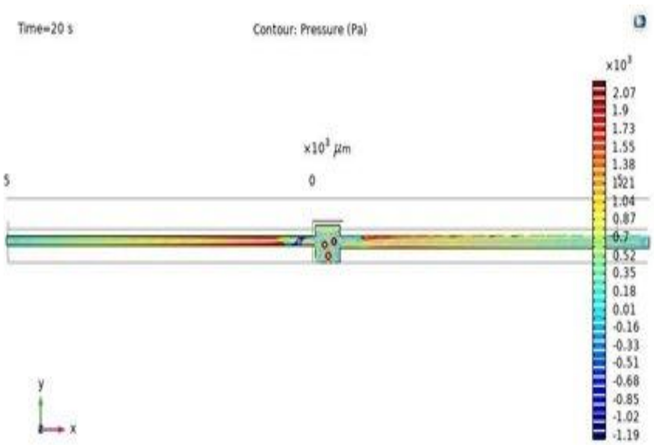

Figure 2 - Fluid pressure trend in microchannels in simulation

Largest inlet fluid pressure value in microchannels is observed at the edges of the microchannel walls. The fluid velocity decreases due to the low volume of fluid inlet, which is due to the decrease in the angle of contact of the fluid surface with the microchannel floor. Inlet fluid pressure field in two-dimensional space is shown in figure .3.

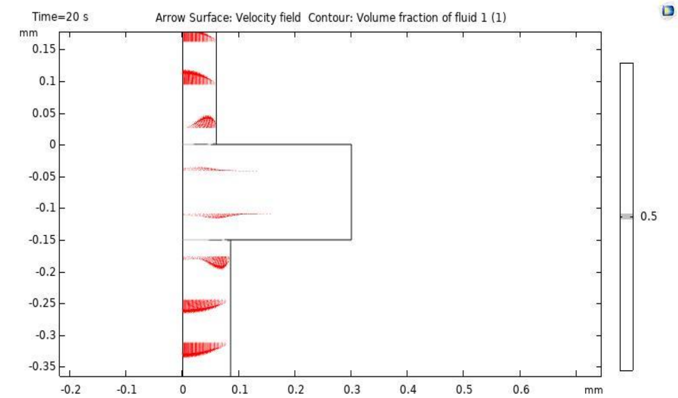

Figure 3. Inlet fluid pressure field in two-dimensional space at the beginning of the

Due to surface tension of the fluid at the beginning of the fluid entry into the microchannels, the maximum fluid velocity is next to the walls, and then the velocity increases in the middle of the microchannels, and then the velocity increases along the walls, as shown in figure 4.

4. Fluid behavior among nanorods:

Fluid behavior in the microchannel is normal in the capillary state without the presence of nanorods and its velocity depends only on the amount of inlet fluid, ambient pressure, and surface material. Now, if we examine the presence of nanorods inside the microchannel, it becomes clear that the fluid velocity is not only dependent on the introduced factors, but also the presence of nanorods inside the microchannel increases the fluid velocity. Since ZnO nano rodsare hydrophilic and the outer surface of the nanorods is also hydrophilic, they pull the Newtonian fluid inside the microchannels. The outer surface energy of the nanorods increases the fluid velocity and more fluid enters the microchannel. The outer surface of the each nanorods provides small capillary force and this effect is multiplied by millions of nanorods in the microchannel, which improves the fluid velocity. As can be seen in the figure 5, the fluid on the flat bed becomes spherical, but at the surface where the nanorods are, the fluid behavior changes, and this introduces the surface hydrophilicity. This is the behavior of the nanorods in the microchannel, which attracts the fluid to the fluid and enters the nanorods. As soon as the fluid enters, the nanorods absorb the fluid through its hydrophilic property and then pass the fluid through the nanorods. The effect of ZnOnanorods on enhancing capillary force is shown in Fig.5.

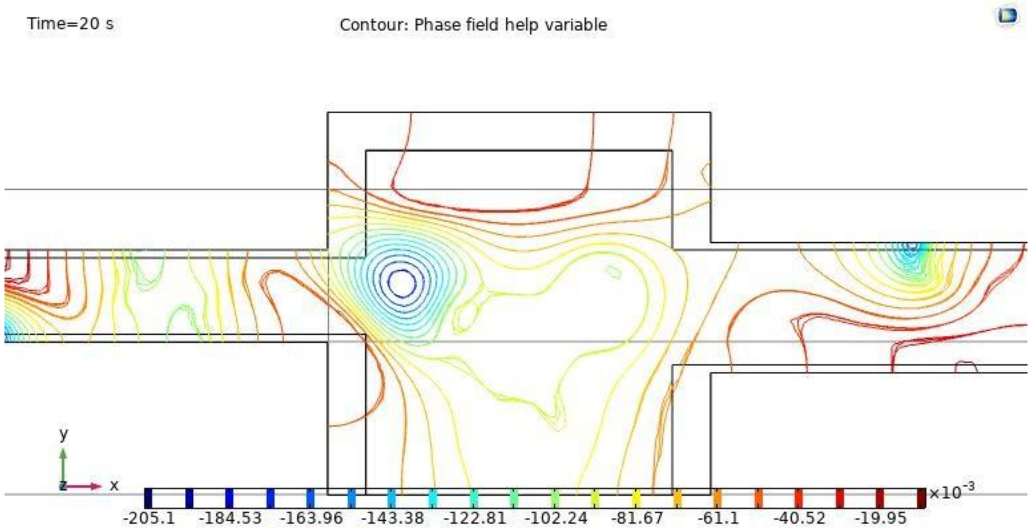

Figure 4. Flow input and flow distribution in microchannels

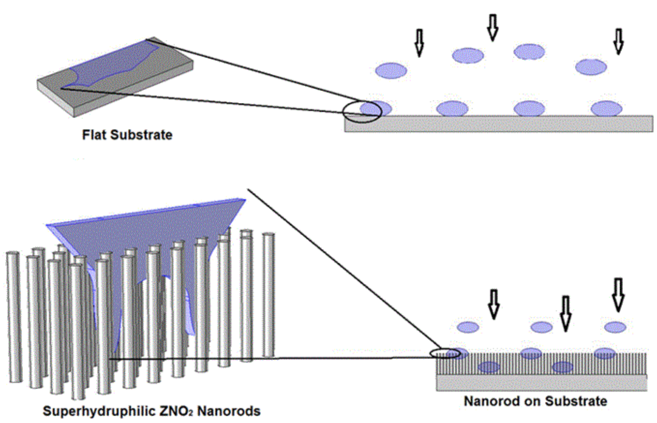

Figure 5. Fluid behavior at the glass substrate coated by titanium oxide nanorods

The effect of ZnO nanords on enhancing capillary force is shown in Figure5. As can be seen in the figure 5, the fluid on the flat bed becomes spherical, but at the surface where the nanorods are, the fluid behavior changes, and this introduces the surface hydrophilicity. This is the behavior of the nanorods in the microchannel, which attracts the fluid to the fluid and enters the nanorods. As soon as the fluid enters, the nanorods absorb the fluid through its hydrophilic property and then pass the fluid through the nanorods.

5. Experimental results:

The original design and the microchannels were created on a laboratory glass slab of 1000 microns thickness. The lithography process was used to create the microchannel on the slide, and then, using BHF acid solution, these microchannels were created on a glass substrate for 20 to 30 minutes. Due to the toxicity of BHF acid soluble gas, it is a very dangerous process.

The fabricated micro structure consists of 16 microchannels with length of 5 mm, widths of 120 microns to 270 microns and depth of 20 microns on glass substrate. It is shown in figure 6.

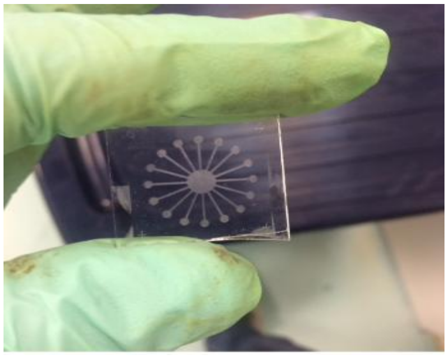

Figure 6. The etched microstructure on the glass

Regarding to standard microfabrication procedure for fabrication of microchannels on glass substrate, photoresist is span on the substrate. Then, the required pattern in transferred from mask to the substrate by exposing the sample to UV light. Finally, the exposed photoresist is developed. The developed pattern is shown in figure 7.

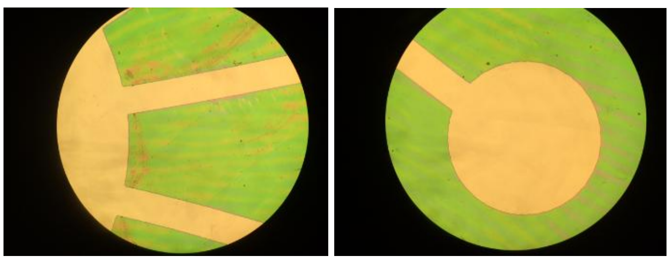

Figure 7. Microchannels after lithography

After lithography, the sample is soaked in BHF to etch some parts of glass and fabricate microchannels. The substrate after BHF etching is shown in figure 8. As mentioned before, the widths of channels are between 120 to 270 microns.

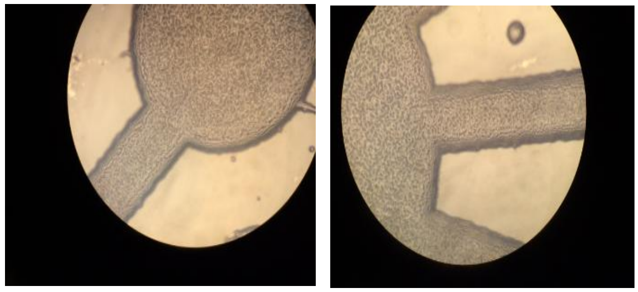

Figure 8. Microchannels after etching in BHF acid solution

To enhance the properties of the capillary phenomena inside the microchannelsZnO nanorodsare grown. The sol-gel method is used to prepare the seed layer. First Monoethanolamine(C_2H_7NO) and 2Methoxy ethanol ($C_3H_8O_2$) are mixed with a ratio of 0.75 mol. Then Zinc acetate dehydrate ($Zn(CH_3COO)_22(H_2O)$) is added and mixed at 90 ° C with a magnetic stirrer to give a clear solgel. The coating is then applied to the substrate and then backed by oven at 270 ° C. Hydrothermal solution is prepared by Zinc nitrate tetra hydrate ($Zn\ (NO_3)_2\ (H_2O)\ _4$) and Ammoniumhydroxide(NH_3OH) (1: 1 ratio) and zinc oxide nanorods are grown on the seed layer at 95 ° C for 2 h. After cooling, the samples were washed by deionized water [20, 21]. Then it is dried in ambient air. Fabrication procedure schematic is shown in figure 9.

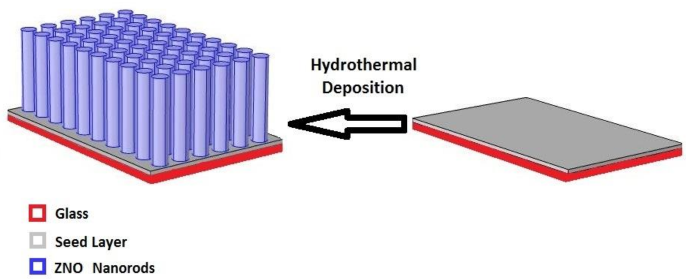

Figure 9. Schematics of growing ZnO nanorods on glass substrate

6. Discussion:

Because of all the aspects of chip testing, various problems during testing and the prevention of microchannel problems, four microchannels were created on each substrate to perform the fluid test within the microchannel. As shown in the following pictures, the Newtonian fluid travels through the microchannel in about 20 seconds. As mentioned earlier, the amount of fluid is also an important parameter in the capillary phenomenon. The following figure shows that the fluid resides spherically on the glass chip which has not any nanorods in microchannels. This is due to the fact that the glass surface is hydrophobic and the angle of contact of the fluid with the chip surface is high. The fluid motion in this chip requires external force. The fluid on the glass chip with nanorods, in contrast to the other chip, is more hydrophilic due to the presence of nanorods and enters the microchannels due to the capillary effect without any external force. The comparison between the microchannels is shown in figure 10.

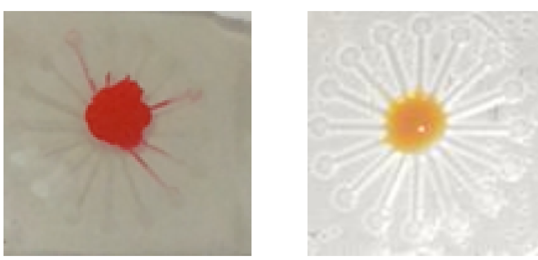

Figure 10 - Left image: Fluid testing on glass with nanorods- Right image: Fluid test on glass without nanorods

As shown in the figure 11, it shows the volume fraction and fluid velocity in the microchannel, which reaches the bottom of the microchannel in 20 seconds. The fluid velocity at the microchannel edges is greater than the middle because of the decrease in the angle of contact of the fluid with the surface of the microchannels. The main reason for the fluid velocity along the walls is that the effect of wettability and hydrophilicity on the walls attracts the fluid to itself and results in increased fluid velocity.

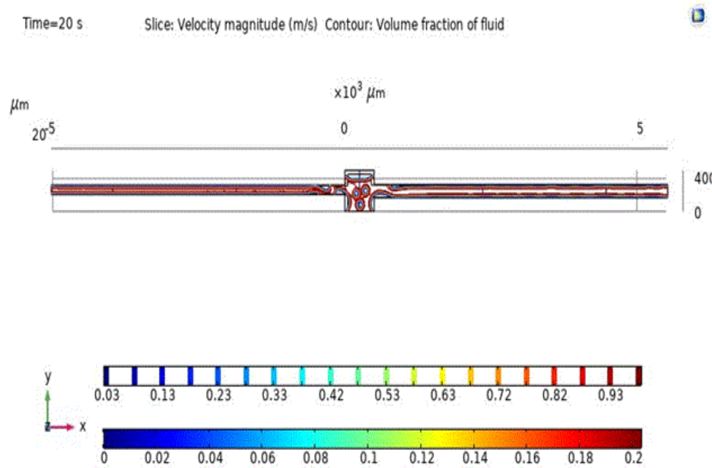

Figure 11 - Illustration of fluid volume fraction and fluid velocity in all microchannel in the simulation

7. Conclusion:

Improvement of aqua solutions motion within microchannels is important in microfluidic devices in order to remove pump section and provide passive fluid motion. In this study, a method was proposed to increase the capillary force for motion of water based solutions in glass microchannels. It can be achieved by increasing surface area and hydrophilicity of microchannels. The aim of this study is enhancement the wettability of the surface of microchannels on glass chips. First, the microchannels on the glass chip were created by chemical etching, then the seed layer was created on the surface, and then ZnO nanorods are grown on the microchannels surface by the hydrothermal method. The effect of coating nanorods on surface was simulated and compared with experimental results. ZnO nanorods are hydrophil and attract aqua solutions to them. Also, the majority of nanorods and their dense nano structure would enhance capillary force and pulls the water alongside of channel. In most of bio researches, the samples are water based solutions. The proposed technique can be applied to glass microstructures in order to make glass more favorite substrate for biological microfluidic researches and applications.

Conflicts of interest

The authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest, or non-financial interest in the subject matter or materials discussed in this manuscript.

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